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DIFLUORAMINE CHEMISTRY

Report Period: 3 April 1961 to 30 June 1961

Thiokol ®

CHEMICAL CORPORATION

REACTION MOTORS DIVISION

DENVILLE, NEW JERSEY

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DIFLUORAMINE CHEMISTRY

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Report RMD-076-Q2-61

Contract NOnr 1878(00)

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3 April 1961 to 30 June 1961

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FOREWORD

This report was prepared by Thiokol Chemical Corporation, Reaction Motors Division, Denville, New Jersey, under Contract No. NOnr 1878(00), ARPA Order No. 186-61. The research reported herein was administered under the direction of the Propulsion Chemistry Branch, Office of Naval Research, with Mr. R. L. Hanson as project engineer.

This quarterly report covers work conducted during the period of 3 April 1961 to 30 June 1961 on RMD Project 076. The following personnel participated in this research:

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ABSTRACT

The chemistry of primary, secondary, and tertiary aliphatic difluoramines is under investigation. In the absence of an α hydrogen, the difluoramino group is surprisingly inert to strong caustic, hydrogen reduction and to reaction with diborane. Dehydrofluorination is the principal reaction of primary and secondary aliphatic difluoramines.

The apparent oxidation of iodide by carbon difluoramines appears to be intimately associated with the dehydrofluorination process. The anomalous stoichiometries observed have been explained on the basis of the hydrofluoric acid accelerated air oxidation of iodide.

Acid permangante oxidation appears to be nonselective and causes extensive fragmentation even with tertiary difluoramines.

Initial attempts to prepare 1,1-bis(difluoramino)cyclohexane were unsuccessful.

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I. INTRODUCTION

The purpose of this program is to investigate the chemistry of the aliphatic difluoramines, and to a lesser extent the organo iminofluorides, and to define the chemical processes which these new functions can undergo. In the first quarterly report, the preparation, purification, and structural characterization of four easily distillable and stable aliphatic bis-difluoramines was described.[1] These were:

I trans 1,2-bis(difluoramino)cyclohexane

II cis 1,2-bis(difluoramino)cyclohexane

III trans 2,5-bis(difluoramino)-2,5-dimethyl-3-hexene

IV 1,2-bis(difluoramino)hexane

Aside from geometrical variations in structure, these particular compounds were chosen for study because they offer examples of three different kinds of carbon difluoramino groups. From these adducts a comparison of the chemical behavior of the NF_2 group when attached to primary, secondary or tertiary carbon atoms can be made, and this should permit us to distinguish the reactions characteristic of the NF_2 group, independent of the presence of an α hydrogen atom.

During the current report period, the study of the interaction of these aliphatic difluoramines with several oxidizing, reducing and solvolytic reagents was pursued. The $C-NF_2$ function, itself, was found to be surprisingly inert and has led to the tentative conclusion that some of the reactions previously associated with this function can be attributed instead to the acid character of an α hydrogen atom and the associated ease of dehydrofluorination.

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II. DISCUSSION

As pointed out previously, our knowledge of the chemical properties of the $C-NF_2$ function is quite meager. No one has bothered to study the behavior of this function to hydrogenation, reduction, oxidation, nucleophilic substitution, and metallation, etc. Prior to the current study, some work has been reported on the tendency of the aliphatic difluoramines to yield fluoride ion under basic conditions and to oxidize iodide to iodine, but neither the reaction products nor the stoichiometry have been well established.

A. Reaction with Basic Reagents

Even weak basic reagents and solvents such as iodide ion and methanol facilitate the dehydrofluorination of primary and secondary aliphatic difluoramines to the corresponding nitrile and fluorimino groups.

$$RCH_2NF_2 \xrightarrow{\text{base}} RC\equiv N$$

$$R_2CHNF_2 \xrightarrow{\text{base}} R_2C=NF$$
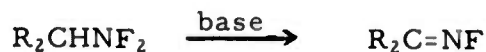
Because of the absence of an α hydrogen, tertiary carbon difluoramines cannot dehydrofluorinate without skeletal rearrangements. It was not surprising, therefore, that the tertiary carbon difluoramines are inert to hot, strongly alkaline reagents as was previously demonstrated with trans 2,5-bis(difluoramino)-2,5-dimethyl-3-hexene (III).[1] This stability of the tertiary functions severely limits the applicability of the alkaline solvolytic method for the quantitative analysis of NF compounds.[2]

The greater stability of the tertiary difluoramines can be the basis of a method of purification. For example, III is formed in high yield from the 1,4 (actually 2,5) addition of tetrafluorhydrazine to 2,5-dimethyl-2,4-hexadiene. However, as previously noted, about 10% of an isomeric product (V) is also formed. Based on an analysis of its infrared spectrum, V was assigned the

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4, 5-bis(difluoramino)-2, 5-dimethyl-2-hexene structure. Because these positional isomers have very similar volatilities and gas chromatographic retention times (3 minute separation), it has been difficult to obtain either adduct completely free of its isomer.

$$(CH_3)_2C=CH-CH=C(CH_3)_2 \xrightarrow{N_2F_4}$$

$$\underset{\substack{| \\ NF_2}}{(CH_3)_2C}-CH=CH-\underset{\substack{| \\ NF_2}}{C}-(CH_3)_2 \quad + \quad \underset{\substack{| \\ F_2N}}{(CH_3)_2C}-\underset{\substack{| \\ NF_2}}{CH}-CH=C(CH_3)_2$$

III 90%   V 10%
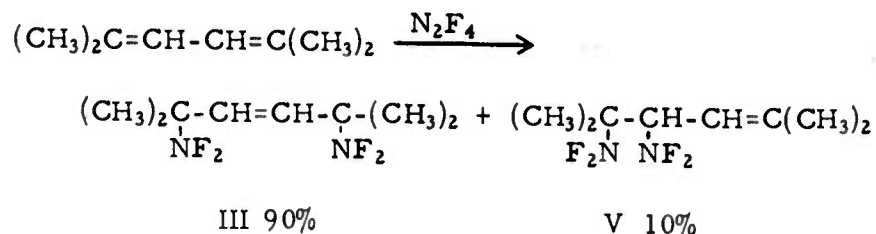
However, taking advantage of the one acidic α hydrogen in V, pure III has been obtained by first converting V with alcoholic caustic to what appears to be 4-fluorimino-5-difluoramino-2, 5-dimethyl-2-hexene (VI) and then resolving the resulting two component mixture by vapor phase chromatography. The retention time for III was unchanged but the separation time at 82°C was now about twenty minutes.

$$\underset{\substack{| \quad | \\ F_2N \ NF_2}}{(CH_3)_2C}-CH-CH=C(CH_3)_2 \quad \longrightarrow \quad \underset{\substack{| \quad || \\ F_2N \ NF}}{(CH_3)_2C}-C-CH=C(CH_3)_2$$

V   VI
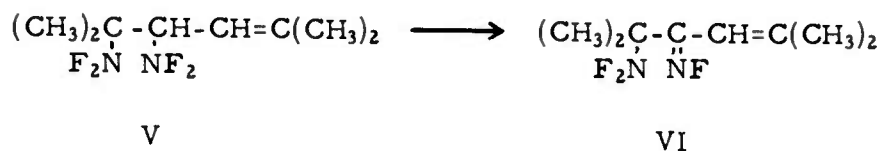
When isolated this way, pure III is a white solid, melting just above room temperature. Its spectrum is shown in Figure 1. Note in Figure 2 (spectrum of fluorimino difluoramine, VI) the shape of the NF peaks at 10.5 μ and 11.5 μ and the appearance of bands in the double bond region near 6 μ and in the skeletal region at 12.5 μ.

  Anal for III Calc: C, 44.85; H, 6.58; F, 35.48; N, 13.08
      Found: C, 44.62; H, 6.99; F, 35.0; N, 12.98

The stability of III to refluxing alcoholic caustic implies that the NF_2 group is not very susceptible to displacement on F or N. This may be due, in part, to a steric factor. Exploratory experiments indicate that III reacts vigorously with phenyl Grignard reagent, a very strong organic base. This latter system is under current investigation.

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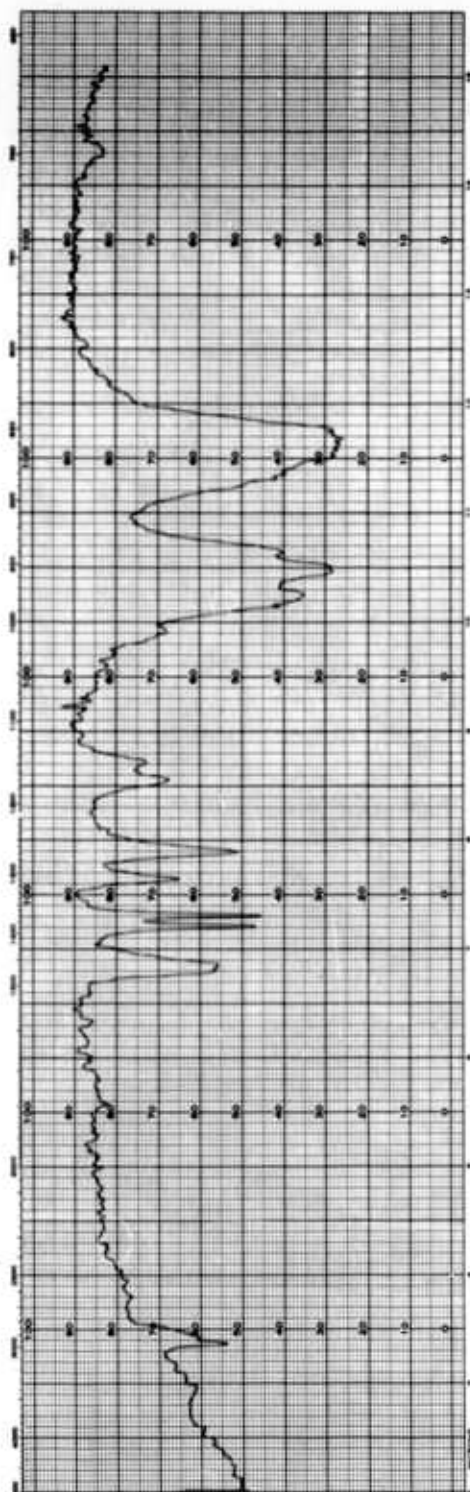Figure 1. Infrared Spectrum of trans 2,5-Bis(difluoramino)-2,5-dimethyl-3-hexene
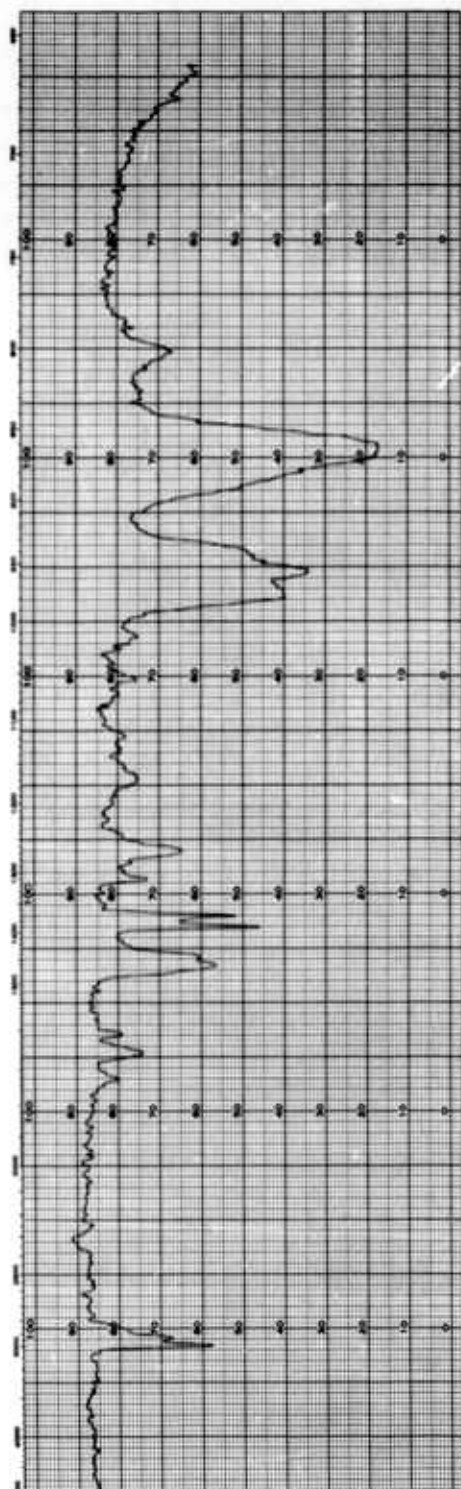
Figure 2. Infrared Spectrum of 4-Fluorimino-5-difluoramino-2,5-dimethyl-2-hexene

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B. Reaction with Iodide Ion

Some laboratories have attempted to utilize the oxidation of iodide to iodine, apparently brought about by various carbon difluoramines in alcohol, acetone or acetonitrile solvent, as a quantitative analytical tool.[2,3] This reaction was assumed to be analogous to the interaction of iodide with N, N-dichloroalkylamines to yield iodine and an azo compound:

$$2 \ RNCl_2 + 4 \ I^- \longrightarrow RN=NR + 2 \ I_2 + 4 \ Cl^-$$

However, the reported results with organic difluoramines were highly erratic. Reproducible and meaningful stoichiometries were obtained infrequently, and in a few cases little or no reaction was observed. It should be emphasized that at times the purity and even the structure of the compounds studied were uncertain. Furthermore, although the fate of the alkyl difluoramine has been postulated, the resultant products have not been isolated.

We had noted that in its rapid oxidation of iodide to iodine in methanol, 1,2-bis(difluoramino)hexane (IV) was mainly converted to a fluorimino hexonitrile, the result of simple dehydrofluorination.[1] The oxidation of iodide appeared to be inexplicable. On the other hand, III would not react with iodide at all. Since III contains only tertiary NF_2 groups, the iodide oxidation by primary and secondary NF_2 appeared to be intimately associated with the dehydrofluorination process. It was suspected that the observed reactions could be attributed, at least in part, to the hydrofluoric acid accelerated air oxidation of iodide:

$$O_2 + 4 \ HF + 4 \ I^- \longrightarrow 2 \ H_2O + 2 \ I_2 + 4 \ F^-$$
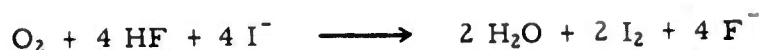
It was easily demonstrated that hydrofluoric acid would effectively accelerate oxidation in an air exposed solution of sodium iodide in methanol or acetonitrile. Even under vacuum line conditions in which air was "rigorously" excluded, a small amount (< 1%) of iodine was formed in a CH_3CN-HF-NaI system. Significantly, only about 9% of the previously observed redox stoichiometry was realized when IV was treated with the CH_3CN-NaI reagent in an air excluded vacuum line.

These results imply that the simple aliphatic bis-difluoramines, at least those being studied here, cannot oxidize iodide directly and that the observed redox reactions are dependent upon a prior dehydrofluorination process. Furthermore, it would appear that a simple secondary fluorimino group, as

in 2-fluoriminohexanonitrile, cannot oxidize iodide either. Since diperfluoro-butyl-N-fluoramine and other hydrogen free organic NF compounds are reported to oxidize substantial quantities of iodide in air excluded systems,[3] it cannot be said that hydrofluoric acid or air is a necessary prerequisite to iodide oxidation. Rather, it seems reasonable to postulate that the presence of two strongly elec-tron withdrawing substituents, such as a perfluoralkyl group, are required to fully develop the oxidizing potential of an NF bond. An electron with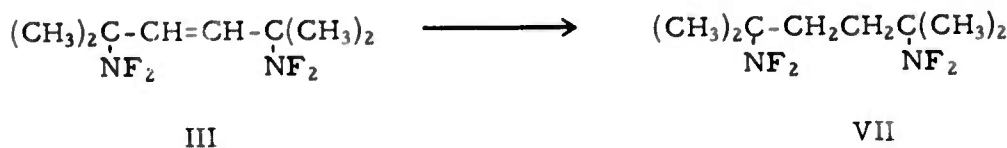drawing substituent could favor the incipient formation of positive and strongly oxidizing fluorine and, therefore, promote a nucleophilic displacement on fluorine by iodide:

$$
\begin{array}{c}
R_fCF_2 \\
\diagdown \\
R_f{}'CF_2
\end{array}
N-F \quad + \quad I^- \longrightarrow
\left[
\begin{array}{c}
R_fCF_2 \\
\diagdown \\
R_f{}'CF_2
\end{array}
\ddot{N}\text{----}F\leftarrow\text{----}I
\right]^-
$$

$$
\left[
\begin{array}{c}
R_fCF_2 \\
\diagdown \\
R_f{}'CF_2
\end{array}
\ddot{N}\colon
\right]
\quad + \quad
\left[\; IF \;\right]
$$

$$\downarrow -F^-$$

$$R_fCF_2\ddot{N}{=}CFR_f{}'$$

$$\downarrow H_2O$$

$$2\ R_fCO_2H \quad + \quad NH_4{}^+ \quad + \quad 5\ F^- \quad + \quad I_2$$

$$\downarrow I^-$$
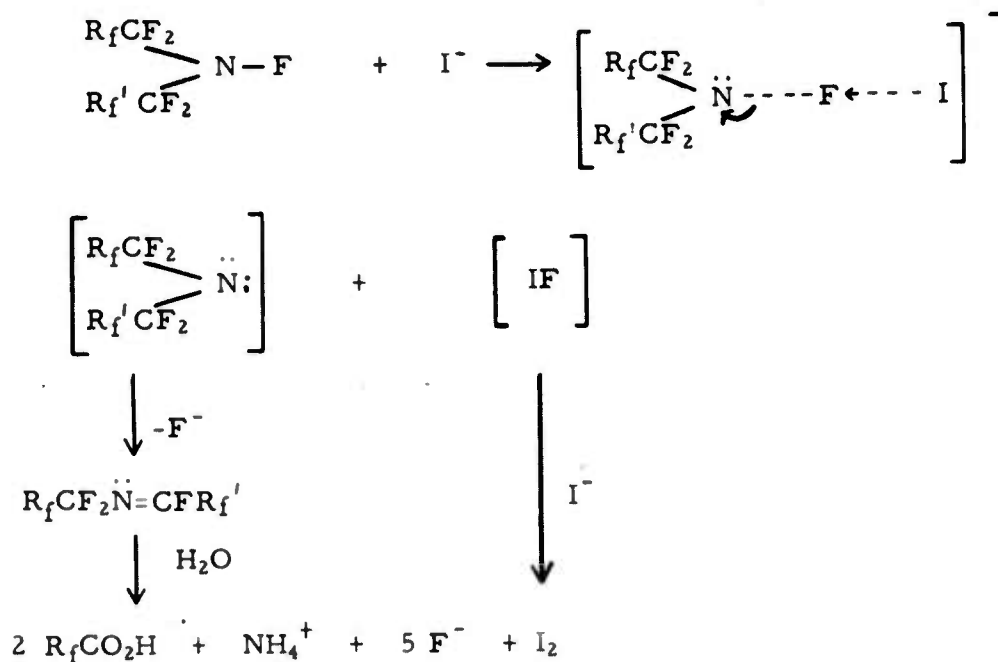
C. Reaction with Reducing Reagents

The saturation of the double bond in III by hydrogen was investigated to eliminate the possibility of allylic activation effects and to determine the stability of the NF$_2$ groups under reducing conditions.

$$
\begin{array}{c}
(CH_3)_2C{-}CH{=}CH{-}C(CH_3)_2 \\
\quad\;|\qquad\qquad\qquad| \\
\quad\;NF_2\qquad\qquad\;\;NF_2
\end{array}
\longrightarrow
\begin{array}{c}
(CH_3)_2C{-}CH_2CH_2C(CH_3)_2 \\
\quad\;|\qquad\qquad\qquad\;| \\
\quad\;NF_2\qquad\qquad\;\;\;NF_2
\end{array}
$$

III   VII

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No uptake of hydrogen was observed when an ethanolic solution of III was treated with hydrogen at a pressure of 66 cm over a paladium on charcoal catalyst. This reaction was repeated under 50 psi hydrogen, but only unchanged III was recovered. The lack of reactivity of the NF_2 group under these conditions is quite significant, but the failure to saturate the double bond may be the result of electronic inhibition.

Reductive hydroboration of III was also attempted.[4] Steric factors should not be paramount in this system, since the sterically related trans ditertiary butyl ethylene has been successfully hydroborated by this method as well as hydrogenated catalytically.[5] The procedure of Brown and Subba Rao[6] for the formation of the intermediate borane (VIII) and the protonolysis procedure of Brown and Murray[7] were employed.

$$III + B_2H_6 \longrightarrow \underset{\underset{NF_2}{|} \quad \underset{BH_2NF_2}{|}}{(CH_3)_2C\text{-}CH_2\text{-}CH\text{-}C\text{-}(CH_3)_2} \xrightarrow{H^+} VII$$
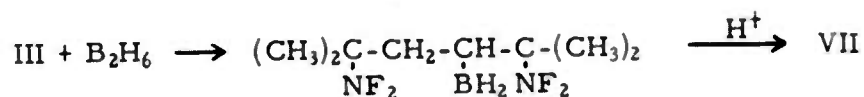
VIII

In the first experiment, the dimethyl ether of diethylene glycol (1-4-1), bp 162°C, was used as the solvent. Diborane was generated in an argon atmosphere by the addition of a slight excess of boron trifluoride ethyl etherate to sodium borohydride. The diborane was then passed into a 1-4-1 solution of the 9:1 mixture of III and VI. The resultant solution was then treated with caproic acid and heated at about 160°C for one hour. Only tars were formed and neither the starting materials nor the desired product could be isolated.

The reaction was repeated under milder thermal conditions using dry dimethyl ether of ethylene glycol (1-2-1), bp 85°C, as solvent and acetic acid as the protonolysis reagent. No reduction was observed, and 92% of the starting mixture of III and VI was recovered. Again, the failure of the NF_2 group to react in the latter experiment is significant. The lack of reactivity of the double bonds in III and VI is probably due to the deactivating effect of the NF_2 group. Since resonance interaction between tertiary difluoramines and a double bond could not be important, the deactivation effect is probably the result of the electronwithdrawing character of the NF_2 group which decreases the ability of the π electron system to donate electrons to a Lewis acid such as BH_3.

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D. Potassium Permanganate Oxidation

It was interesting to observe that all four bis-difluoramines (I, II, III, and IV) reacted with potassium permanganate in aqueous acetic acid. I and II reacted slowly to give, in addition to unreacted starting materials, fluoride ion and a water soluble oxidation product, assumed to be adipic acid. III and IV reacted rapidly. Since I, II, and IV dehydrofluorinate readily, it was not clear whether the observed reduction of permanganate was due to the NF_2 group itself or to an unsaturated intermediate. We had previously demonstrated the reduction of permanganate by aqueous difluoramine.[8] The oxidation of III was studied, and an attempt was made to isolate the olefin oxidation product, α-difluoramino-isobutyric acid, VIII.

The olefin mixture of III and VI was treated with the stoichiometric amount of potassium permanganate in aqueous acetic acid. The reaction was rapid and apparently complete. However, only water soluble reaction products, including about 13% fluoride ion were isolated. A large amount (ca 34%) of the starting olefin mixture was recovered. The ratio of III to VI in the recovered material was still about 9:1, suggesting a nonselective oxidation.

The data at hand indicate that the NF_2 group is being directly attacked by permanganate. However, the possibility still exists that the oxidation of III results in the formation of the acid, VIII, and that this in turn decarboxylates and dehydrofluorinates to products which can be lost by further oxidation or volatilization. Currently, the same oxidation is being studied in basic media. In pyridine, the oxidation of III proceeds rapidly and exothermically, but the nature of the oxidation products has not been determined.

E. Condensation Reactions

The lability of the α hydrogen atom in primary and secondary difluoramines suggests the possible utilization of the anion, IX, as a synthetic intermediate.

$$R_2CHNF_2 \longrightarrow (R_2CNF_2)^- \longrightarrow R_2C=NF + F^-$$

IX

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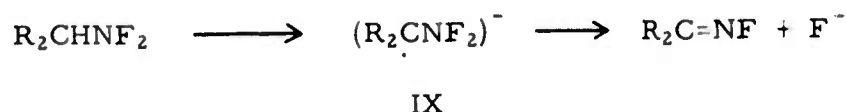
If the elimination of fluoride ion is subsequent to and not simultaneous with the removal of a proton, then the anion, IX, might be a useful intermediate for certain addition and metathetical reactions. Even though resonance stabilization is unlikely, IX bears a formal resemblance to a nitroalkane anion. Therefore the feasibility of effecting aldehyde and Michael type condensations with primary and secondary alkyl difluoramines is under investigation. It also appears possible that the direct nitration of the alkyl difluoramines as well as a Shechter-Kaplan redox nitration [9] of the anion might also be feasible.

Preliminary exploratory experiments have been conducted between IV and p-nitrobenzaldehyde. No apparent reaction occurred in benzene or benzene methanol solutions; however, a slow reaction was observed when pyridine was added to a benzene solution of the reagents.

F. Preparation of Bis-difluoramine

The recent discovery of the conversion of aldehydes and ketones to 1,1-bis-difluoramines in a sulphuric acid-difluoramine system [10] should prove to be a very useful tool for the development of organic difluoramine chemistry. In particular, it would be of great interest to compare the chemical behavior of 1,1-bis(difluoramino)cyclohexane, X, with its isomers, I and II. However, two attempts to prepare X by the published procedure have failed. Nevertheless, this synthesis and similar ones will be pursued.

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III. EXPERIMENTAL

A. trans 2,5-Bis(difluoramino)-2,5-dimethyl-3-hexene

1. Preparation

In a typical experiment, a 2 liter bulb was charged with 2.75 grams (25 mmoles) of 2,5-dimethyl-2,4-hexadiene and 32 mmoles of tetrafluorohydrazine. The bulb was heated at 120-140°C for four hours. The excess tetrafluorohydrazine was then pumped off, and the residue was vacuum distilled into a Dry Ice trap and collected.

The crude product, 5.0 grams, previously shown to be a mixture of III and V, was refluxed in 150 ml of a 1:1 ethanol-water solution containing 15 grams (0.37 mole) of sodium hydroxide. The mixture was then diluted with 1 liter of water and extracted with ethyl ether. The ether extract was washed with water until neutral, dried over anhydrous sodium sulfate, filtered and distilled. The product was vacuum distilled, bp 94°C/35 mm, to give a 55-85% yield of III and VI, n_D^{23} 1.4094. Vapor phase chromatography easily separates III and VI; the separation time at 82°C is about 20 minutes. Integration of the two chromatographic peaks gives a 9:1 ratio of III to VI.

2. Attempted Hydroboration and Protonolysis

In a previously flame dried apparatus and under an argon atmosphere, • diborane was generated from 0.2 gram (0.005 mole) of sodium borohydride in 20 ml of the dimethyl ether of ethylene glycol (1-4-1) by the addition of 1.2 ml (0.006 mole) of boron trifluoride ethyl etherate. The diborane thus generated was passed into a solution of 1.07 grams (0.005 mole) of the 9:1 mixture of III and VI in 20 ml of 1-4-1. One ml of caproic acid was added. The solution was slowly heated to 160°C and held there for one hour. Insoluble tars were formed, and the remaining solution did not contain either the desired product or the starting material.

This reaction was repeated using 10 ml of dimethyl ether of ethylene glycol (1-2-1) solvent, and employing 4.28 grams (0.02 mole) of the mixture of III and VI as the reagent. Diborane (0.01 mole) was generated as previously described, and protonolysis was attempted using 2 ml of glacial acetic acid. The solution was heated at 90°C for sixteen hours. The resulting

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orange-brown solution was diluted with water and extracted with ethyl ether. The ether extract was washed with water and then dried over anhydrous sodium sulfate. Removal of solvent in vacuo left 3.9 grams (92%) of liquid, identified by gas chromatography and infrared spectroscopy as the unaltered starting mixture.

2. Oxidation with Permanganate

A 0.7 M solution of potassium permanganate in 3:1 acetic acid-water was added dropwise with stirring to a solution of 4.28 grams (0.02 mole) of the 9:1 mixture of III and VI in 20 ml of glacial acetic acid. Immediate bleaching of the purple color and formation of manganese dioxide was noted. The additive was stopped after 76 ml (0.053 mole) of the permanganate reagent had been added. The mixture was extracted with ethyl ether. The ether extract was washed with a sodium bicarbonate solution. About 1.5 grams of a water insoluble liquid was isolated which proved to be the original starting mixture. The recovery was 35%. Analysis of the aqueous phase showed the presence of 0.01 mole of fluoride ion, 12.5%.

B. 1,2-Bis(difluoramino)hexane and Methanolic Sodium Iodide in Air

A solution composed of 1.88 grams (0.01 mole) of 1,2-bis(difluoramino)-hexane (IV) and 6.0 grams (0.04 mole) of sodium iodide in 20 ml of methanol was allowed to stand at 20°C, exposed to the air, for one day. At the end of this time, all the iodide had been converted to iodine as shown by the titration of an aliquot with standard thiosulfate. The reaction mixture was then diluted with 100 ml of water; the iodine was reduced with sodium sulfite. Then the reaction mixture was extracted with ethyl ether. The ether extract was dried over sodium sulfate, filtered and distilled. The residual oil was vacuum distilled to give 0.3 gram, bp $61-2^{\circ}$C/30 mm. Vapor phase chromatography separated the distillate into one major component, identified as 2-fluorimino-hexanonitrile, and two unidentified components.

C. 1,2-Bis(difluoramino)hexane and Sodium Iodide in Aqueous Acetonitrile

A thoroughly degassed solution of 10 grams (0.067 mole) of sodium iodide in 10 ml of water and 80 ml of acetonitrile was prepared in the vacuum line. This solution was added to 0.188 gram (0.001 mole) of 1,2-bis(difluoramino)-hexane and the resulting solution was stirred under its own vapor pressure for 19 hours. After dilution with water and acidification with acetic acid, the iodine liberated was titrated with standard thiosulfate. The titration showed that 0.000179 mole of iodine (9% yield) had been produced.

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IV. FUTURE WORK

1. Prepare and characterize the gem aliphatic bis-difluoramines.

2. Study Michael and aldehyde type condensations with primary and secondary difluoramines.

3. Study the direct and redox nitration of primary and secondary difluoramines.

4. Study the interaction of aliphatic difluoramines with organometallic reagents.

5. Study the oxidation of organic difluoramines.

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V. REFERENCES

1. Thiokol Chemical Corporation, Reaction Motors Division, RMD 076-Q1-61, March 1961.

2. Rohm and Haas, P-59-6 II, March 31, 1959.

3. Minnesota Mining and Manufacturing Co., Report No. 4, March 31, 1960; Summary Report on High Energy Propellants, April 30, 1959

4. H. C. Brown, Tetrahedron, 12, 117 (1961).

5. T. J. Logan and T. J. Flautt, J. Am. Chem. Soc., 82, 3446(1960);

   F. L. Howard, T. W. Mears, A. Fookson, P. Pomerantz, J. Am. Chem. Soc., 60, 2171(1946).

6. H. C. Brown and B. C. Subba Rao, J. Am. Chem. Soc., 81, 6428(1959).

7. H. C. Brown and K. J. Murray, J. Am. Chem. Soc., 81, 4108(1959).

8. Thiokol Chemical Corp., Reaction Motors Division, RMD-2075-F1, December 31, 1960.

9. R. B. Kaplan and H. Shechter, Abstracts, Symposium on Nitro Aliphatic Chemistry, Lafayette, Ind., May 25-26, 1961, pg. 1.

10. K. Baum, Aerojet-General Corp., "Gem-Difluoramino Compounds," Special Report, Contract NOnr 2655(00), March 1961.